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16. ABSTRACT

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COMPARISON OF PHOTOCHEMICAL BEHAVIOR OF VARIOUS HUMIC SUBSTANCES IN WATER: III. SPECTROSCOPIC PROPERTIES OF HUMIC SUBSTANCES

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ABSTRACT -- Spectral absorption coefficients and fluorescence quantum efficiencies were determined for humic substances from a variety of sources. Specific absorption coefficients k_h, for humic substances at wavelengths λ from 300 to 500 nm can be closely described by the relation $Ae^{B(450-\lambda)}$, where A and B are constants. When the k_h values are in units of liter (mg organic carbon)$^{-1}$meter^{-1} and wavelength λ is in nanometers, mean values of A and B for aquatic humus in the 12 water bodies studied were 0.6±0.3 and 0.014±0.001, respectively. Spectral absorption coefficients of dissolved organic matter in blackwater rivers, of the "yellow substance" in the sea, and of fulvic acids extracted from soils are very similar. Fluorescence quantum yields of humic substances were low and more variable than the absorption coefficients, ranging from 0.0005 to 0.012 with excitation at 350 nm (average of 0.0045±0.0038 for 6 waters). Fluorescence spectra for the humic substances were remarkably similar with maximum emission at 430 to 470 nm. Results of this study can be used to compute photolysis rates of pollutants as a function of depth in natural water bodies.

INTRODUCTION

A major portion of the organic matter in the aquatic environment comprises humic substances called "aquatic humus," "yellow substances," and other names (1). Aquatic humus imparts a yellow to brown color to water and, along with suspended sediments and pigmented microorganisms, is one of the most important sunlight absorbers in natural waters. The concentration of aquatic humus is sufficiently high in some inland water bodies that the water actually looks black. Recent studies have indicated that aquatic humus in air-saturated natural water can photosensitize the oxidation of certain aquatic pollutants and biologically important substances (2). Spectroscopic properties of the humus in the water are related to the photosensitized oxidation rates, with the highest rates observed in natural waters that most strongly absorb light (2). Carey found that the photosensitized reaction rate of the pesticide, 2,4-D, in several natural waters was related to the fluorescence of the substances in the water (3).

A number of studies concerning light absorption and fluorescence properties of humic substances in general and aquatic humus in particular have appeared in the literature. Efforts to quantitate light absorption by soil-derived humic substances have been discussed by Schnitzer and Khan (4) and by Flaig and co-workers (5). Visible light absorption by aquatic humus has been quantitated in units of color, based on a platinum cobalt standard, and fair correlations between color and total organic carbon (TOC) have been reported (1). Others have found correlations between ultraviolet absorption and TOC (6) in inland and coastal waters. Højerslev (7), Jerlov (8),Stuermer (9), and Takematsu (10) have all examined the absorption properties of the dissolved organic matter in the sea.

Efforts also have been made to relate the fluorescence from natural waters to TOC. Smart et al. (11) found a good relationship between fluorescence intensity and TOC for natural water samples from diverse sources in Great Britain. Earlier studies by Black and Christman (2), however, had led to the conclusion that the organic carbon to fluorescence ratio for natural waters was not constant. Højerslev (7) has likewise reported that the yellow substance to fluorescence ratio is not constant in coastal waters except for well-mixed areas. Smart et al. (11) and Ghassemi and Christman (13) obtained very similar fluorescence spectra for the natural waters that they studied. Most of the fluorescence is derived from natural substances, although fluorescent whitening agents may contribute in some highly polluted waters (14). Several studies have appeared concerning fluorescence of natural organic substances in the ocean (8,15).

The above studies suggest that both the absorption and fluorescence properties of the dissolved organic matter are similar from one natural water to another. Few quantitative data are available, however, to compare the spectroscopic properties of humic substances obtained from soils, natural waters, and commercial sources. In this paper, spectral absorption coefficients and fluorescence quantum yields are presented for a variety of humic substances. These data, along with the photolysis rate comparisons (16), are being used to assess the ability of humic substances from various sources to simulate the photosensitizing action of aquatic humus.

EXPERIMENTAL

Materials. Sources of the natural water samples and the humic substances are described elsewhere (2,16). All solutions were centrifuged at high speeds as previously described (16) to remove light-scattering particles prior to obtaining the spectral data.

Equipment. Absorption spectra were obtained on a Perkin Elmer Model 602 digital spectrophotometer. Fluorescence spectra were obtained with a Farrand Model 801 Spectrofluorometer. Organic carbon concentrations were measured using a Beckman Model 915 Organic Carbon Analyzer. Degassing of solutions was accomplished by four freeze-thaw cycles on a high-vacuum rack.

Fluorescence Measurements. Solutions of humic substances were prepared as previously described (16). Fluorescence quantum yields were determined as described elsewhere (17), employing air-saturated solutions except where noted. Solutions of the humic substances or the natural water and solutions of quinine sulfate in 0.1 N H_2SO_4 were optically matched at 350 nm (absorbance equalled 0.25 in a 10.00 cm cell). The quinine sulfate solution was diluted by a factor of 100 to obtain a solution whose fluorescence caused a photomultiplier response in the same range as that of the solutions of humic substances. The fluorescence spectra were corrected, and areas under the true fluorescence spectra were integrated using a planimeter. The fluorescence quantum efficiency, ϕ_f, of a humic substance was computed using the equation

$$\phi_f = \phi_q \frac{(I_f)_h}{(I_f)_q} \qquad (1)$$

where $(I_f)_h/(I_f)_q$ is the ratio of areas under the true emission spectra of the humic solution and the quinine sulfate solution and ϕ_q is the fluorescence quantum efficiency of quinine sulfate, known to equal 0.55 (17). Removal of oxygen by degassing of the Aucilla River or Okefenokee Swamp water caused no change in ϕ_f.

RESULTS AND DISCUSSION

Absorption. The electronic absorption spectra of the dissolved commercial humic acids were similar to spectra of fulvic acids isolated from soils and to spectra of natural water samples that contained high concentrations of aquatic humus, as evidenced by their yellow coloration. The spectra had no apparent absorption bands but rather had continuous absorption that increased with decreasing wavelength in the visible and ultraviolet region. All of the solutions were found to obey Beer's Law in the concentration range of 1 to 40 mg/liter of total organic carbon. Specific absorption coefficients, k_h, for the humic substances [in liters (mg org C)$^{-1}$ meter $^{-1}$] were computed using Eq. 2.

$$k_h = \frac{2.303\ A_\lambda}{C_o\ \ell} \qquad (2)$$

where A_λ = absorbance in meters^{-1} at wavelength λ
C_o = concentration of dissolved organic matter in mg organic carbon/liter
ℓ = cell pathlength in meters

Absorption coefficients were determined for dissolved organic matter in several natural waters and for humic substances extracted from soils, including some commercial humic acids (Tables 1 to 3, Figure 1). Considering the diversity of sources, the range of k_h values at a given hydrogen ion concentration (pH) was remarkably small. The soil-derived humic acids absorb more strongly than the fulvic acids and the dissolved organic matter. Absorption coefficients of the organic substances in the blackwater samples (Aucilla River, Okefenokee Swamp, Econfina River, Fenholloway River) were the same, within a factor of two, as the k_h values for the soil humic substances. Also of interest is the similarity in specific absorption coefficients of humic acids extracted from soils in various parts of the world (Table 2). Somewhat lower k_h values were observed in natural waters that had lower concentrations of organic substances (Table 1).

Table 1. Specific absorption coefficients, k_h, of dissolved organic carbon in natural water samples and of humic substances extracted from soils.

Source of Organic Carbon	pH	Dissolved Organic Carbon mg/l	k_h, l(mg Org.C)$^{-1}$m^{-1} 366nm	465nm
Fluka Humic Acid	6.0	11	4.3	1.6
Aldrich Humic Acid	6.0	8.0	5.8	1.7
Karl Roth Humic Acid	6.0	8.1	5.6	2.30
Fulvic Acid - NC Soil	6.0	15	3.0	0.73
Fulvic Acid - CA Soil	6.0	15	3.1	0.75
Aucilla River	6.0	18	2.5	0.53
Fluka Humic Acid	11	11	4.4	1.8
Aldrich Humic Acid	11	8.0	5.9	1.9
Karl Roth Humic Acid	11	8.1	6.6	2.4
Fulvic Acid - CA Soil	11	15	3.7	1.1
Aucilla River, Lamont, FL	11	18	3.3	0.70
St. Marks River, St. Marks, FL	8.7	9.0	2.5	0.75
Okefenokee Swamp, Waycross, GA	4.1	24	2.0	
Econfina River, Perry, FL	4.2	30	3.6	
Fenholloway River, Foley, FL	7.7	77	3.7	
Gulf of Mexico, Live Oak Island, FL	8.3	6	1.0	
Wakulla River, Wakulla Springs, FL	8.6	6	0.4	
Hickory Hills Pond, Athens, GA	7.2	4	1.0	
Mississippi River, Baton Rouge, LA	8.3	14	0.4	

Changes in pH caused varying effects on the absorption coefficients (Table 1). The k_h values generally increased in changing from pH 6.0 to pH 11.0 (Table 1), but the increase was larger in the case of the organic substances in the river and the fulvic acids than in the

Table 2. Specific absorption coefficients, k_h, for dissolved humic acids at pH 11 and 465 nm.

Source of Organic Carbon	k_h, l(mg Org. C)$^{-1}$m^{-1}
Fluka Humic Acid	1.8
Aldrich Humic Acid	1.9
Karl Roth Humic Acid	2.4
Fulvic Acid - CA Soil	1.1
Aucilla River, Lamont, FL	0.70
Humic Acid - Sod Podzolic[a]	0.92
Humic Acid - Gray Forest[a]	2.46
Humic Acid - Ordinary Chernoum[a]	2.51
Humic Acid - Meadow Solonetz[a]	1.70
Humic Acid - Serozem[a]	1.84
Humic Acid - Brown Mountain Forest[a]	1.50
Humic Acid - Mountain Meadow[a]	2.21
Humic Acid - Shallow Red Soil[a]	1.91
Humic Acid - Cinnamon Brown Soil[a]	1.40

[a]Data of Orlov concerning humic acids from Soviet soils (19).

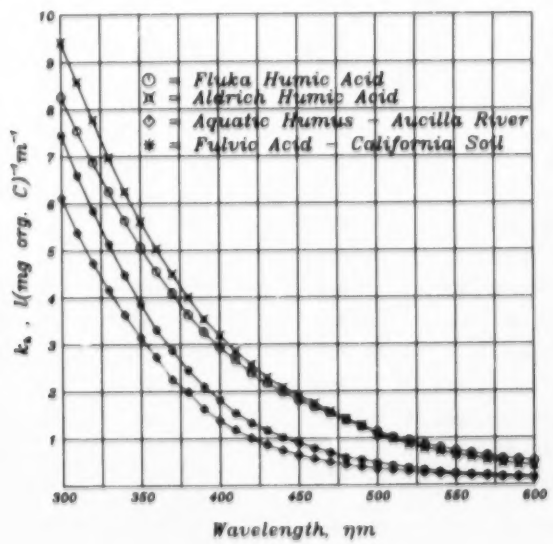

Figure 1. Absorption spectra of various humic substances in water at pH 6.0.

case of the humic acids. Also, the pH effect was larger at longer than at shorter wavelengths. In no case did the observed increase in k_h exceed a factor of 50% in changing from pH 6 to pH 11. These pH effects have been noted elsewhere (4,5) and are possibly attributable to ionization of phenolic and/or carboxyl groups.

The appearance of the absorption spectra of various humic substances (Figure 1) suggested that the decrease in k_h with increasing wavelength might be exponential. Indeed, spectral data from 300 to 500 nm could be closely described by Equation 3.

$$k_h = A\, e^{B(450-\lambda)} \qquad (3)$$

where A and B are constants, and λ is the wavelength in nanometers.

Values of A and B for several humic substances are listed in Table 3. Højerslev (7) has also applied a similar equation to describe absorption coefficients of yellow substances in coastal

Table 3. Parameters that apply to computation of spectral values of specific absorption coefficients for various humic substances, k_h, where $k_h = Ae^{B(450-\lambda)}$ liter(mg Org. C)$^{-1}$m^{-1}. (λ is the wavelength in nanometers.)

Source of Humic Material	pH	B	A	r^2 (No. of Values)
Fluka humic acid	6.0	0.0100	1.86	0.993 (31)
Aldrich humic acid	6.0	0.0104	1.90	0.999 (31)
Roth humic acid	6.0	0.0104	1.52	0.999 (31)
Humic acid - mean values		0.0102±0.0002	1.76±0.21	
Fulvic Acid - NC Soil	6.0	0.0146	0.861	0.997 (31)
Fulvic Acid - CA Soil	6.0	0.0139	0.909	0.999 (31)
Contech Fulvic Acid	6.0	0.0128	0.623	0.996 (28)
Fulvic acid - mean values		0.0138±0.009	0.80±0.15	
Aucilla River, Lamont, FL	6.0	0.0147	0.680	0.999 (31)
Okefenokee Swamp, Waycross, GA	4.1	0.0145	0.634	0.999 (31)
Suwanee River, FL		0.0140	[a]	0.996 (31)
Fenholloway River, Foley, FL	7.7	0.0134	1.09	0.996 (31)
St. Marks River, St. Marks, FL	8.7	0.0116	0.780	0.998 (16)
Quincy Bog, Tilton, NH	5.2	0.0150	[a]	0.994 (31)
Williamson River, Klamath Agency, OR	6.6	0.0152	0.382	0.999 (31)
Ogeechee River, Savannah, GA	6.5	0.0175	[a]	0.996 (31)
Econfina River, Perry, FL	4.2	0.0152	0.702	0.998 (31)
Freshwater aquatic humus - mean values		0.0145±0.0017	0.71±0.26	
Gulf of Mexico, St. Marks, FL	8.1	0.0151	0.249	0.998 (16)
North Sea[b]	8.1	0.0140	0.42	
Gulf of Mexico, near Tampa, FL[c]		0.0149	[a]	0.952 (13)
Marine aquatic humus - mean values		0.0147±0.0006	0.33±.09	
All aquatic humus - mean values		0.0145±0.0014	0.60±0.28	

[a]Not determined.
[b]Computed from data of Højerslev (7) assuming yellow substance contains 50 by weight of organic carbon.
[c]Computed from diffuse attenuation coefficients (320 to 380 nm) for Gulf of Mexico near Tampa (20).

waters of the North Sea. Values of B for soil fulvic acids, freshwater humic substances, and yellow substances in the sea from various parts of the world are nearly the same, at least in this limited data set. For the 12 natural waters included in this study, mean values of B and A are 0.014±0.001 and 0.6±0.3, respectively. Baker (17), however, through a similar analysis of spectral data for other dissolved organic substances in the sea (7-10), has found values of B that are somewhat larger than those shown in Table 3. Values of B for the soil humic acids were about 40% smaller than for soil fulvic acids and for the dissolved organic substances in the natural waters included in Table 3, and the values of A are somewhat larger.

Fluorescence. Fluorescence spectra were also found to be similar for the commercial humic acids, fulvic acids, and the humus in the various natural water samples (Figure 2). Maximum emission with excitation at 350 nm occurred in the 430 to 470 nm wavelength region with shoulders at 400-420 nm and 500-520 nm. These spectra are similar to those reported by Ghassemi and Christman (9), Smart et al. (7), and Jerlov (8) for dissolved organic matter in natural waters. Fluorescence quantum efficiencies for the various humic substances were determined by comparison to the emission from quinine sulfate in 0.1 N H_2SO_4 (12) (Table 4). The quantum yields were low in all cases with emission from the humic acids being somewhat less efficient (average 0.00093±0.00038) than from the organic matter in the natural water (average 0.0045±0.0037) and the soil fulvic acids (average 0.0017±0.0006). Considering the diversity of sources of the humic substances in Table 4, the fluorescence quantum yields and the spectra are remarkably similar. One exception was the water from the Everglades in South Florida. The organic matter in this water emitted more intensely and at somewhat shorter wavelengths (maximum at 430 nm) than the organic matter in the other natural waters included in this study. Removal of dissolved air by careful degassing had no effect on the fluorescence efficiency of aquatic humus in the Aucilla River water, although such effects are often observed with other organic compounds such as polycyclic aromatic hydrocarbons.

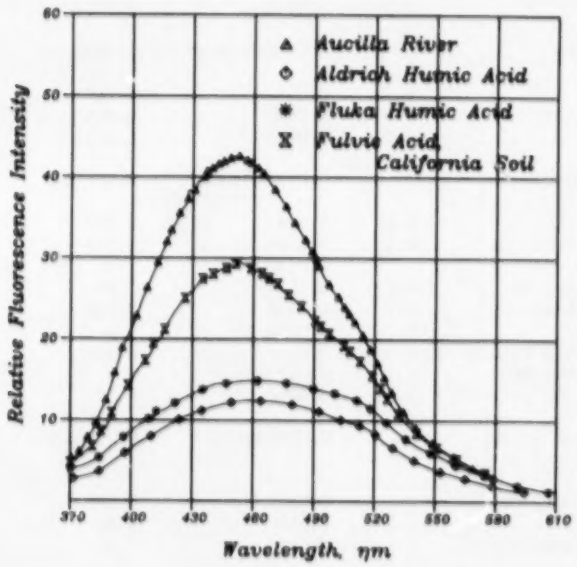

Figure 2. Fluorescence spectra of humic substances in water (excited at 350 nm; pH 6.0).

Table 4. Quantum yields for fluorescence, ϕ_f, of humic materials excited at 350 nm[a].

Source of Humic Materials	pH	Wavelength of Maximum Emission, nm	$\phi_f \times 10^3$
Aucilla River, Lamont, FL	6.0	450	3.3
Okefenokee Swamp, Waycross, GA	4.0	450	2.7
Quincy Bog, NH	5.4	445	1.6
Williamson River, Klamath, OR	6.8	445	4.1
Ogeechee River, Savannah, GA	6.5	450	3.4
Everglades, South FL	7.4	430	12
Fulvic Acid, Contech	6.0	450	1.1
Fulvic Acid, isolated from California soil	6.0	450	2.3
Aldrich Humic Acid	6.0	450	1.2
	11.0	450	1.0
Karl Roth Humic Acid	6.0	430	0.5
Fluka Humic Acid	6.0	460	1.1

[a]Determined by relative fluorescence measurements as described by Parker and Rees (17) employing quinine sulfate in 0.1 N H_2SO_4 as standard.

SUMMARY

To summarize these results, a close similarity was found between the electronic absorption and fluorescence spectra of humic and fulvic acids and aquatic humus. Limited data indicate a close similarity between the spectral absorption coefficients of the yellow substance in the sea, the humic substances in several freshwater bodies, and fulvic acids extracted from soils (all were the same within a factor of two). A recent report by Bricaud and co-workers (21) provides much more extensive confirmation of the striking similarity in the wavelength dependence of light absorption by yellow substance and the humic substances included in this study. Although still unexplained, the remarkable similarity between the spectroscopic properties of various humic substances lends further support to our earlier suggestion (16) that commercial humic substances may be useful as model photosensitizers in tests designed to evaluate environmental hazards of chemicals.

Results of this study also improve the ability to compute photolysis rates of pollutants in natural waters. Through application of the general relationships (eq. 2,3) determined here, the abundant data concerning organic carbon concentrations in natural waters can be used to approximately calculate the solar spectral irradiance (7, 20), and thus the photolysis rate constants of aquatic pollutants (22), as a function of depth.

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